

# PATENT SPECIFICATION

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## (54) METHOD AND COMPOSITIONS FOR TREATING THE HAIR AND SKIN BASED ON COPOLYMERS CARRYING TERTIARY AMINE AND/OR QUATERNARY AMMONIUM GROUPS

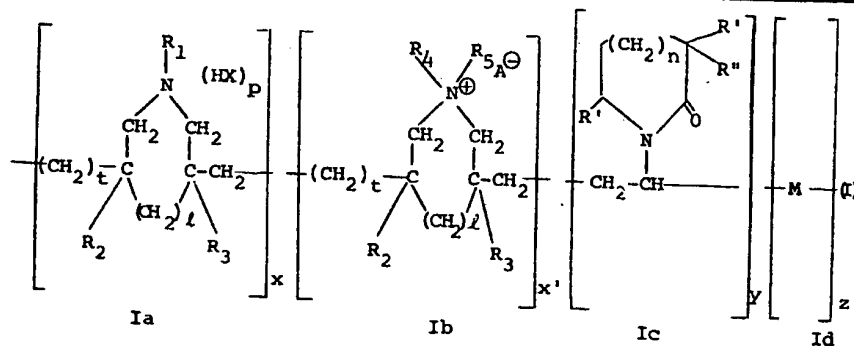
(71) We, L'OREAL, a joint stock company constituted under the French law, of 14, rue Royale 75, Paris, 8eme, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to cosmetic compositions based on copolymers containing tertiary amine and/or quaternary ammonium groups, and to their use for the care of the hair and skin.

It was proposed some years ago to use certain copolymers containing tertiary amine and/or quaternary ammonium groups for the care of the hair and skin. In fact, it was found that these copolymers had a certain affinity for hair keratin and skin and consequently they made it possible to avoid a certain feeling of dryness and roughness of the hair and skin. However, these copolymers are incompatible with certain cosmetic compositions, and consequently their use has been considerably restricted. Furthermore, the affinity of these copolymers is not sufficiently lasting and, consequently, it is necessary to carry out renewed applications with increasing frequency in order to give the skin and hair a natural appearance which is pleasant to the eye and to the touch.

The surprising discovery has now been made, according to the present invention, that, by using a different class of copolymers carrying tertiary amine and/or quaternary ammonium groups, it is possible, on the one hand, to obtain a wide variety of formulations without encountering the disadvantages found with the previous copolymers, and, on the other hand, to obtain a lasting effect, taking into account the higher affinity towards hair keratin and skin of the copolymers used according to the invention.

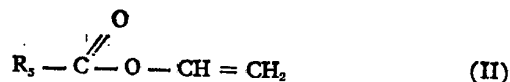
The present invention provides a method of treating the skin or hair which comprises applying thereto a cosmetic composition suitable for the care of the hair and skin, which composition contains, in an appropriate cosmetic carrier, at least one copolymer carrying tertiary amine and/or quaternary ammonium groups, the said copolymer corresponding to the following general formula:



in which each of  $\text{R}_1$ ,  $\text{R}_4$  and  $\text{R}_5$ , which are identical or different, represents an alkyl radical having from 1 to 12 carbon atoms, each of  $\text{R}_2$  and  $\text{R}_3$ , which are identical or different, represents a hydrogen atom or a methyl radical, each of  $\text{R}'$  and  $\text{R}''$ , which are identical or different, represents a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms,  $l$  is 0 or 1 such that if  $l = 0$ ,  $t = 1$  and if  $l = 1$ ,  $t = 0$ ,  $n$  is 0, 1 or 2,  $p$  is 0 or 1,  $\text{A}$  represents an anion, preferably a chloride or bromine ion,  $\text{HX}$  is an inorganic or organic acid, preferably hydrochloric acid, hydrobromic acid, acetic acid or lactic acid, and  $\text{M}$  represents a recurring unit of a polymerisable unsaturated monomer,  $x+x'$  corresponding to 95—5 mol%, it being possible for  $x$  or  $x'$  to be 0,  $y$  corresponding to 5—95 mol%, and  $z$  corresponding to 0—60 mol%,  $(x+x') + y + z$  being equal to 100 mol%.

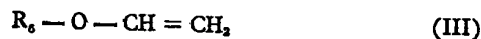
Amongst the unsaturated monomers which can give rise to the units of the formula  $\text{M}$  (Id), there may be mentioned, in particular:

(i) the vinyl esters of the formula:



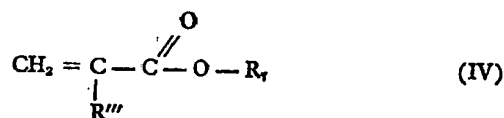
in which  $\text{R}_5$  represents an alkyl radical having from 1 to 17 carbon atoms,

(ii) the vinyl ethers of the formula:

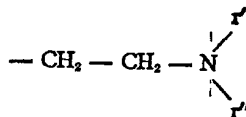


in which  $\text{R}_6$  represents an alkyl radical having from 1 to 16 carbon atoms,

(iii) the acrylic or methacrylic esters of the formula:

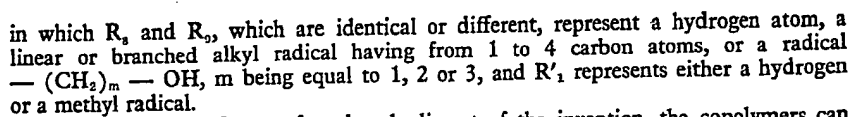


in which  $\text{R}'''$  represents either a hydrogen atom or a methyl radical and  $\text{R}_7$  represents a linear or branched alkyl radical having from 1 to 18 carbon atoms, an alkyl radical having from 1 to 3 carbon atoms which is substituted by at least one alkoxy having from 1 to 4 carbon atoms, or a radical of the formula:



in which  $\text{r}'$  and  $\text{r}''$ , which are identical or different, represent an alkyl radical having from 1 to 4 carbon atoms, and

5



According to a first preferred embodiment of the invention, the copolymers can be represented by the following:



in which:  $R_1, R_2, R_3, R', R'', M, HX, l, t, p$  and  $n$  are as defined above,  $x$  corresponding to 95–5 mol%,  $y$  corresponding to 5–95 mol% and  $z$  corresponding to 0–60 mol%.

According to a second preferred embodiment of the invention, the copolymers can be represented by the following general formula:



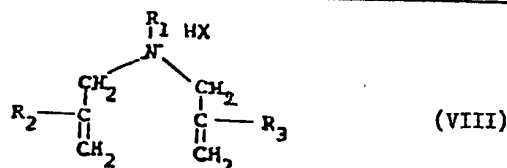
in which:  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R'$ ,  $R''$ ,  $M$ ,  $A$ ,  $l$ ,  $t$  and  $n$  are as defined above,  $x'$  corresponding to 95–5 mol%,  $y$  corresponding to 5–95 mol% and  $z$  corresponding to 0–60 mol%.

According to a third preferred embodiment of the invention, the copolymers can simultaneously contain units (Ia) and (Ib) in addition to the units (Ic) and optionally the units (Id).

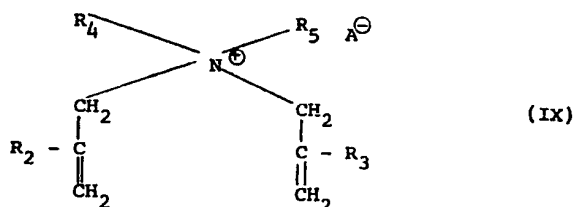
The copolymers which can be used according to the invention exhibit the particular characteristic of being soluble both in water and in alcohols, especially ethanol and isopropanol.

These copolymers usually have a weight average molecular weight of 2,000 to 500,000, preferably from 4,000 to 75,000.

The units (Ia) of the copolymers can be obtained by the cyclopolymerisation of a salified diallylalkylamine having the following formula:



in which:  $R_1$ ,  $R_2$ ,  $R_3$  and  $HX$  are as defined above, and the units (Ib) of the copolymers can be obtained by the cyclopolymerisation of a quaternary ammonium salt, and especially of a diallyldialkylammonium chloride or bromide having the following formula:



in which:  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$  and  $A$  have the same meaning as above.

In fact, during the polymerisation of these diallyl compounds of the formulae (VIII) and (IX) with a N-vinyl lactam giving rise to units (Ic), either alone or mixed with another monomer, the compounds cyclise to give to the units (Ia) and (Ib) respectively, which have either five or six members in the ring.

Amongst the salified diallylalkylamines of the formula (VIII), there may be mentioned, in particular: the hydrochlorides, hydrobromides, acetates and lactates of methylallylamine, ethylallylamine, butylallylamine, octylallylamine, decylallylamine and dodecylallylamine.

Amongst the diallyldialkylammonium chlorides or bromides of the formula (IX), there may be mentioned, in particular: dimethylallyl ammonium, methylethylallyl ammonium, methylbutylallyl ammonium and methyl dodecylallyl ammonium chlorides or bromides.

Amongst the N-vinyl lactams which give rise to the units of the formula (Ic), there may be mentioned, in particular, N-vinylpyrrolidone-2, N-vinylpiperidone-2, N-vinylcaprolactam, N-vinyl-5-methylpyrrolidone-2 and N-vinyl-3,3-dimethylpyrrolidone-2. Preferably N-vinylpyrrolidone-2 is used.

Amongst the unsaturated monomers which give rise to the units M (Id) capable of being polymerised with the diallyl monomer and N-vinyl lactam, there may be mentioned, in particular:

i) amongst the vinyl esters of the formula (II): vinyl acetate, vinyl propionate, vinyl butyrate, vinyl laurate and vinyl stearate,

(ii) amongst the vinyl ethers of the formula (III): methyl vinyl ether, ethyl vinyl ether, isopropyl vinyl ether, ethylhexyl vinyl ether, dodecyl vinyl ether and hexadecyl vinyl ether,

(iii) amongst the acrylates and methacrylates of the formula (IV): methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, 2-methylbutyl, 3-methylbutyl, 2-ethylbutyl, amyl, 3-methylhexyl, 3-ethylhexyl, 2-ethylhexyl, 2-methoxyethyl and 2-ethoxyethyl acrylates and methacrylates, as well as 2-(N,N-dialkylamino)-ethyl acrylates and methacrylates and especially 2-(N,N-dimethylamino)-ethyl and 2-(N,N-diethylamino)-ethyl acrylates and methacrylates, which are optionally quaternised by means of dimethyl sulphate, ethyl bromide or any other quaternising agent, and

(iv) amongst the acrylamides and methacrylamides of the formula (V): acrylamide, methylacrylamide, N-methylacrylamide, N-tert-butylacrylamide, N-hydroxymethylacrylamide, N-(1,1-dimethyl-2-hydroxy)-ethyl-1-acrylamide and N,N-dimethyl, N,N-diethyl-, N,N-dibutyl- and N,N-diisobutyl-acrylamides and -methylacrylamides.

Certain of the copolymers which can be used in the compositions are known and their preparation is described in U.S. Patent No. 3,862,091.

The other copolymers can be obtained in accordance with the same method of operation by copolymerisation in emulsion or in solution in water or in an organic

liquid such as ethanol, methanol, benzene, toluene or xylene.

The polymerisation catalysts which are generally used can be conventional, such as hydrogen peroxide, benzoyl peroxide and azo-bis-isobutyronitrile, but preferably t-butyl peroxyvalate or t-butyl hydroperoxide.

5 The polymerisation reaction can also be initiated by irradiation or by oxidation/reduction systems such as the hydrogen peroxide/ferrous chloride or ammonium persulphate/ferrous chloride couples.

10 The polymerisation is generally carried out at a temperature of 30 to 150°C, and preferably 60 to 90°C.

When it is desired to obtain polymers of the formula VI in which the units Ia are in the form of free amines, the polymers obtained in the form of a salt can be treated at ambient temperature with a base such as sodium hydroxide.

The cosmetic compositions which contain the copolymers can be in various forms.

15 The cosmetic compositions used in the invention can contain the copolymers of the formula (I) either as the principal active ingredient or as an additive.

Furthermore, these compositions generally contain at least one adjuvant usually employed in cosmetic compositions.

20 The cosmetic compositions can be in the form of, for example, aqueous, alcoholic or aqueous-alcoholic solutions (the alcohol being especially a lower (i.e. of 1 to 6 carbon atoms) alkanol such as ethanol or isopropanol), or in the form of creams, gels or emulsions or also in the form of aerosols in which a propellant is present, packaged in a container.

25 The adjuvants which are generally present in the cosmetic compositions according to the invention are, for example, perfumes, colorants, preservatives, stabilisers, softening agents, emulsifiers, sequestering agents and thickeners as well as sunlight filters. The compositions which contain one or more of such adjuvants are novel and form another aspect of the present invention.

30 It is appropriate to point out that the cosmetic compositions according to the invention are either compositions which are ready for use or concentrates which can be diluted before use.

The cosmetic compositions according to the invention are not therefore restricted to a particular concentration range of the copolymer of the formula (I).

35 The concentration of copolymers of the formula I in the cosmetic compositions is generally from 0.01 to 15% by weight, and preferably from 0.1 to 10% by weight.

40 As indicated previously, the copolymers of the formula (I) exhibit valuable cosmetic properties, especially when they are applied to the hair. Thus, when they are applied to the head of hair, either by themselves, or together with other active substances in the case of a treatment such as shampooing, dyeing or wavsetting, they markedly improve the qualities of the hair and restore, in particular, suppleness and an attractive sheen.

45 Furthermore, they assist the treatment and facilitate the disentangling of wet hair. In contrast to the copolymers previously used for this purpose, they do not make dry hair heavy and they therefore make it easier to obtain bulky hairstyles. Furthermore, they make an effective contribution to eliminating the deficiencies of hair which has been sensitised by chemical treatments or by degradation caused by the atmosphere, the sun or by bathing in the sea.

50 The copolymers used in the compositions are of particular value when they are used as pre-treatment agents, especially with an anionic and/or non-ionic shampoo or before an oxidative colouration which is itself followed by an anionic and/or non-ionic shampoo. The hair is then particularly easy to comb out and has a very soft feel. They can also be used as pre-treatment agents in other operations for treating the hair, for example in permanent waving operations.

55 The cosmetic compositions for the hair can be in the form of, for example, aqueous, alcoholic or aqueous-alcoholic solutions (the alcohol being, for example, ethanol or isopropanol) or in the form of creams, gels or emulsions or also in the form of sprays. In this last case, the compositions are usually packaged in an aerosol container in which a propellant such as nitrogen, nitrous oxide, carbon dioxide or a fluorochlorinated hydrocarbon such as those known under the Registered Trade Mark "Freon", or mixtures of such propellants, are present.

60 The adjuvants which are generally present in the cosmetic compositions for the hair, according to the invention are, for example, perfumes, colorants, preservatives, sequestering agents, thickeners, emulsifiers or hair resins.

The cosmetic compositions for the hair are therefore, in particular:

a) treatment compositions characterised in that they contain, as an active ingredient, at least one polymer of the formula I in aqueous or aqueous-alcoholic solution.

The proportion of polymer of the formula (I) is generally from 0.01 to 15% by weight, and preferably from 0.1 to 8% by weight.

The pH of these lotions is in the region of the neutral point and can vary, for example, from 6 to 8.

If necessary, the pH can be brought to the desired value by adding either an acid, such as citric acid, or a base, in particular an alkanolamine such as monoethanolamine or triethanolamine.

In order to treat the hair with such a lotion, the said lotion is typically applied to the wet hair and allowed to act for 3 to 15 minutes and the hair is then rinsed.

If desired, the hair can then be set in waves.

b) shampoos characterised in that they contain at least one polymer of the formula I and a cationic, non-ionic or anionic detergent.

Suitable cationic detergents are, in particular, long-chain quaternary ammonium compounds, esters from fatty acids and aminoalcohols, or amine polyethers.

Suitable non-ionic detergents are, in particular, esters of polyols and of sugars, the products resulting from the condensation of ethylene oxide with fatty materials, with long-chain alkylphenols, with long-chain mercaptans or with long-chain amides, and polyethers of polyhydroxylic fatty alcohols.

Suitable anionic detergents are, in particular, the alkali metal salts, the ammonium salts or the amine or aminoalcohol salts of fatty acids such as oleic acid, ricinoleic acid and the acids of copra oil or of hydrogenated copra oil, the alkali metal salts, the ammonium salts or the aminoalcohol salts of the sulphates of fatty alcohols, in particular of  $C_{12}$ — $C_{14}$  and  $C_{16}$  fatty alcohols, the alkali metal salts, the magnesium salts, the ammonium salts or the aminoalcohol salts of the sulphates of oxyethyleneated fatty alcohols, the products resulting from the condensation of fatty acids, for example, isothionates, taurine, methyltaurine or sarcosine, alkylbenzenesulphonates, in particular those in which the alkyl is  $C_{12}$ , alkylaryl-polyether-sulphates and monoglyceride-sulphates.

All these detergents, as well as numerous other detergents, are well known and are described in the literature.

In the form of shampoos, these compositions can also contain various adjuvants such as, perfumes, colorants, preservatives, thickeners, foam stabilisers or softening agents or also one or more cosmetic resins.

In these shampoos, the concentration of detergent is generally from 5 to 50% by weight and the concentration of copolymer of the formula (I) is generally from 0.01 to 15%, and preferably 0.1 to 5%, by weight.

c) wavesetting lotions, in particular for sensitised hair, characterised in that they contain at least one polymer of the formula (I) in aqueous, alcoholic or aqueous-alcoholic solution.

The concentration of copolymer of the formula (I) in these wavesetting lotions is generally from 0.1 to 5%, and preferably from 0.2 to 3%, by weight.

The pH of these wavesetting lotions is generally from 3 to 9, and preferably from 4.5 to 7.5.

d) dyeing compositions for the hair, characterised in that they contain at least one polymer of the formula (I), a colorant and a carrier. The carrier preferably consists of a cream.

The concentration of the polymers of the formula (I) in these dyeing compositions is generally from 0.5 to 15% by weight, and preferably from 0.5 to 10% by weight.

In the case of an oxidative colouration, the dyeing composition can be packaged in two parts, the second part typically being hydrogen peroxide. The two parts are mixed at the time of use.

e) lacquers for the hair, characterised in that they contain an alcoholic or aqueous-alcoholic solution of at least one copolymer of the formula (I), which is optionally associated with another resin, this solution being placed in an aerosol container and mixed with a propellant which is liquefied under pressure.

An excellent aerosol lacquer can be obtained, for example, by mixing at least one copolymer of the formula (I) with an anhydrous aliphatic alcohol such as ethanol or isopropanol and with a propellant or with a mixture of propellants such as those listed above.

In these compositions, the concentration of copolymers is generally from 0.5 to 3% by weight.

Of course, as for the previous types of composition, it is possible to add various ingredients, such as colorants or plasticisers, to these lacquers.

f) pre-treatment compositions which are, in particular, in the form of aqueous or aqueous-alcoholic solutions, optionally in aerosol flasks, or in the form of creams or gels, these pre-treatment compositions being intended for application to the hair before a shampoo, especially before an anionic or non-ionic shampoo, before an oxidative coloration followed by an anionic and/or non-ionic shampoo or also before a permanent-waving treatment.

In these pre-treatment compositions, the copolymer of the formula (I) forms the active ingredient and its concentration is generally from 0.1 to 15%, and in particular from 0.2 to 8%, by weight.

The pH of these compositions is in the region of the neutral point and is generally from 3 to 9 and, in particular, from 6 to 8.

These pre-treatment compositions can contain various adjuvants such as plasticisers, perfumes and colorants.

According to a variant, the copolymers of the formula (I) are used, in cosmetic compositions for the hair, in association with other polymers, of anionic or cationic character.

According to this embodiment, the polymer of anionic or cationic character is generally present in the composition at a concentration of 0.01 to 10%, and preferably 0.2 to 5%, by weight.

As indicated above, the cosmetic compositions can also be used for treating the skin. In fact, such compositions make it possible to facilitate hydration of the skin and therefore prevent it from drying out. In addition, these compositions make it possible to give the skin an excellent softness to the touch.

Such cosmetic compositions are preferably in the form of creams, gels, emulsions or aqueous, alcoholic or aqueous-alcoholic solutions.

The concentration of the copolymer of the formula (I) in these compositions for the skin is generally from 0.1 to 15% by weight, and preferably from 0.2 to 6% by weight.

The adjuvants which are generally present in these cosmetic compositions are, for example, perfumes, colorants, preservatives, thickeners, sequestering agents, emulsifiers and sunlight filters.

These compositions for the skin constitute especially treatment creams or treatment lotion for the hands or face, or alternatively anti-sunburn creams, tinted creams, make-up removal milks, foam-bath liquids or also deodorant compositions. These compositions can be prepared using conventional methods.

For example, in order to obtain a cream, an aqueous phase containing, in solution, the copolymer of the formula (I) and, optionally, other ingredients or adjuvants can be emulsified with an oily phase.

The oily phase can comprise various compounds such as paraffin oil, Vaseline (Registered Trade Mark for liquid petrolatum), sweet-almond oil, avocado oil, olive oil, and fatty acid esters such as glyceryl monostearate, ethyl or isopropyl palmitates, and alkyl myristates such as propyl, butyl or cetyl myristates. Fatty alcohols such as cetyl alcohols or waxes such as beeswax can also be added.

The copolymers of the formula (I) can be present in the cosmetic compositions for the skin either as an additive or as a main active ingredient.

The following Examples further illustrate the present invention; Examples 1 to 62 illustrate the preparation of the polymers which do not, in themselves, form part of the invention.

## EXAMPLES OF THE PREPARATION OF THE COPOLYMERS.

### EXAMPLE 1.

30 g (0.145 mol) of dimethyldiallylammonium bromide, 100 g of water and a solution of 1.2 g of t-butyl hydroperoxide in 70 g (0.524 mol) of N-vinylpyrrolidone-2 are introduced into a 1 litre round-bottomed flask equipped with a mechanical stirrer and nitrogen inlet. The reaction mixture is heated to 70°C and kept at this temperature for 24 hours, whilst stirring. It is allowed to cool and the solution is then poured dropwise into 3 litres of acetone. The polymer which has precipitated is filtered off and dried at 40°C under reduced pressure.

Yield: 70%.

## EXAMPLE 2.

25 g (0.225 mol) of N-vinylpyrrolidone-2, 38 g (0.242 mol) of 2-(N,N-dimethylamino)-ethyl methacrylate and 37 g (0.179 mol) of dimethyldiallylammonium bromide are copolymerised in the presence of 1 g of t-butyl hydroperoxide, in accordance with the method of operation of Example 1.

After precipitation and drying, the polymer is obtained with a yield of 56%.

Examples 3 to 52 are summarised in Tables I to III which follow.

These copolymers were prepared in accordance with the method of operation of Example 1, using the solvents and precipitation agents or other means of purification indicated in the Tables.

For all these Examples, t-butyl hydroperoxide was used as the catalyst, with the exception of Example 24 in which azo-bis-isobutyronitrile was used.

The compositions are expressed in molar fractions.

The symbols used in the Tables have the following meanings:

- a : water
- a\* : emulsion in water
- a\*\* : cold water
- b : ethyl alcohol
- c : methyl alcohol
- d : acetone
- e : petroleum ether
- f : acetonitrile
- g : dialysis



TABLE I

EXAMPLES	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Dimethyldiallyl ammonium bromide	0.45	0.5	0.2	0.4	0.5	0.2	0.65	0.45	0.45	0.8	0.8	0.5	0.48	0.75	0.3	0.5	0.65	0.3	0.4
N-Vinylpyrrolidone-2	0.1	0.05	0.2	0.2	0.3	0.7	0.25	0.45	0.45	0.6	0.05	0.35	0.40	0.10	0.6	0.4	0.3	0.2	0.4
2-(N,N-Dimethylamino)-ethyl methacrylate	0.45		0.6																
2-(Methacryloyloxy)-ethyl-1-trimethyl-ammonium methylsulphate		0.45		0.4	0.2	0.1	0.1	0.1	0.1	0.1					0.1				
Lauryl methacrylate																			
Isopropyl methacrylate											0.15	0.15							
Butyl methacrylate													0.12						
Vinyl acetate														0.15		0.1			
Vinyl laurate																			
Vinyl stearate																	0.05		
Vinyl butyrate																			
Cetyl vinyl ether																			
Isopropyl vinyl ether																		0.5	0.2
Acrylamide	a	a	a	a	a	a	b	b	b	a	b	b	b	b	b	b	c	a	a
SOLVENT																			
PRECIPITANT	d	d	d	d	d	d	d	e	e	d	f	d	d	f	d	d	f	d	d
YIELD %	40	50	60	65	60	45	35	30	25	30	34	23	28	32	40	30	20	40	34

TABLE II

EXAMPLES	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38
Dimethyldiallylammonium bromide	0.2	0.4	0.3	0.3	0.7	0.45	0.25							0.40			
Methylbutyldiallylammonium bromide								0.20	0.20		0.35				0.20	0.20	
Methyloctyldiallylammonium bromide												0.20					
Methyldecyldiallylammonium bromide													0.35		0.20	0.20	
Methyldodecyldiallylammonium bromide										0.20							0.20
N-Vinylpyrrolidone-2	0.4	0.3	0.3	0.4	0.1	0.50	0.50	0.50	0.50	0.70	0.50	0.70	0.30	0.40	0.20	0.55	0.60
N-tert-Butylacrylamide	0.2										0.10	0.05	0.05	0.10	0.05		
2-(N,N-Dimethylaminol)-ethyl methacrylate	0.2						0.25	0.30	0.30	0.10	0.05	0.05	0.30			0.25	0.20
Vinyl acetate		0.1									0.05			0.10			
Methacrylamide			0.4	0.3		0.05											
N-Hydroxymethacrylamide																	
Methyl acrylate		0.2			0.2										0.55		
2-(Methacryloyloxy)-ethyl-1-trimethylammonium methyl sulphate																	
N-(1,1-Dimethyl-2-hydroxy)-ethyl-1-acrylamide																	
SOLVENT	b	a	a	a	a	a	b	b	b	b	b	b	b	b	b	b	a*
PRECIPITANT or other purification	d	d	d	d	d	d	g	g	g	g	d	d	d	d	f	g	a**
YIELD %	29	20	25	20	18	18	20	22	19	25	28	20	25	40	30	25	27

TABLE III

EXAMPLES	39	40	41	42	43	44	45	46	47	48	49	50	51	52
Methylbutyldiallylammonium bromide		0.40												
Methyloctyldiallylammonium bromide			0.20	0.20										
Methyldodecyldiallylammonium bromide	0.25				0.80	0.90	0.80	0.20				0.3	0.7	0.13
Dimethyldiallylammonium bromide														
Diallylmethylammonium hydrochloride									0.20					
Diallylbutylammonium hydrochloride										0.30				
Diallyloctylammonium hydrochloride											0.20			
Diallyldodecylammonium hydrochloride												0.7	0.3	0.55
Diallyldodecylammonium hydrochloride														
N-Vinylpyrrolidone-2	0.30	0.45	0.15	0.15	0.20	0.05	0.10	0.80	0.80	0.70	0.80	0.7	0.3	0.55
Lauryl methacrylate		0.05	0.05											
Stearyl methacrylate				0.20		0.05								
Acrylamide	0.1						0.10							0.22
N-tert.-Butylacrylamide														
2-(N,N-Dimethylamino)-ethyl methacrylate	0.30													
2-(Methacryloyloxy)-ethyl-1-trimethylammonium methyl-sulphate		0.10	0.60	0.45										
SOLVENT	a	b	b	a	a	a	b	a	a	a	a	a	a	b
PRECIPITANT OR OTHER PURIFICATION	g	d	f	f	d	d	d	g	g	g	g	g	g	e
YIELD %	25	34	40	20	30	25	20	25	25	30	30	32	28	46

## EXAMPLE 53.

Preparation of the copolymer of Example 44 in unsalified form.

10 g of the copolymer prepared in accordance with Example 44 are dissolved in 100 g of water at ambient temperature, whilst stirring. 0.1N sodium hydroxide is added to this solution until the pH of the solution is between 12 and 13. Stirring is continued for 1 hour and the solution is then filtered. The polymer is collected in the form a white precipitate. Yield: 40%.

## EXAMPLES 54 and 55.

In accordance with the same method of operation as that described in Example 53, the polymers of Examples 43 and 45 were also obtained in the unsalified form, with a final yield of between 35 and 60%.

## EXAMPLES 56 to 62.

The polymers of Examples 46 to 52 are treated under the same conditions as those described in Example 53 above; however, the solutions obtained are not filtered but are evaporated to dryness under reduced pressure at 50°C. The residues are then taken up with acetone, the solution is filtered and the polymers are isolated after evaporation of the acetone. Yield: about 30 to 35%.

## COMPOSITION TABLES.

## EXAMPLE A.

A treatment composition which is intended for application after shampooing is prepared according to the invention by mixing the following ingredients:

	Vaseline oil	15 g	
25	Cetyl/stearyl alcohol	2.5 g	25
	Cetyl/stearyl alcohol polyoxyethyleneated with 10 mols of ethylene oxide	2.5 g	
	Copolymer obtained in accordance with Example 1	1.2 g	
	Water q.s.p.	100 g	
30	The pH of this composition is 4.4.		30
	This composition is applied to the wet hair for a few minutes and the hair is then rinsed. The hair thus becomes very easy to comb out and is glossy and easy to style.		
35	In this example, the polymer obtained in accordance with Example 1 can be replaced by the same amount of one of the polymers prepared in accordance with Examples 4, 5 to 8 and 46 to 52.		35

## EXAMPLE B.

A wavesetting lotion is prepared according to the invention by mixing the following ingredients:

40	Copolymer obtained in accordance with Example 2	1.5 g	40
	Ethyl alcohol	50 g	
	Perfume	0.1 g	
	Colorant	0.4 g	
	Water q.s.p.	100 g	
45	The pH of this composition is 5.		45
	After application of this lotion, the hair is easy to comb out and it is glossy, full of life and not charged with static electricity.		

In this example, the polymer obtained in accordance with Example 2 can advantageously be replaced by the same amount of one of the polymers prepared in accordance with Examples 9 to 15 and 34 to 42.

#### EXAMPLE C.

- 5 A wavesetting lotion is prepared according to the invention by mixing the following ingredients: 5

	Copolymer obtained in accordance with Example 3	0.5 g	
10	Quaternary polyvinylpyrrolidone copolymer having a molecular weight of 100,000 marketed under the Registered Trade Mark "Gafquat 734" by Messrs. General Aniline	0.5 g	10
	Quaternised cellulose sold under the name "JR 400" Messrs. Union Carbide	0.3 g	
	Ethyl alcohol q.s.p.	15 g	
15	Perfume	0.3 g	15
	Colorant	0.2 g	
	Water q.s.p.	100 g	

The pH of this composition is adjusted to 8.

- 20 When applied to bleached hair, this wavesetting lotion makes the wet hair very easy to comb out. After drying the hair, an excellent waveset is obtained, the hair being soft to the touch, glossy and easy to style. 20

In this example, the polymer obtained in accordance with Example 3 can be replaced by the same amount of one of the polymers prepared in accordance with Examples 16 to 25, 44 and 45.

#### EXAMPLE D.

- 25 A brushing lotion is prepared according to the invention by mixing the following ingredients: 25

	Copolymer obtained in accordance with Example 4	0.6 g	
	Trimethylcetylammmonium bromide	0.2 g	
30	Perfume	0.2 g	30
	Colorant	0.4 g	
	Water q.s.p.	100 g	

The pH of this composition is 6.5.

- 35 This lotion is applied to natural hair dried by the brushing technique. The passage of the brush is facilitated and the dry hair is soft, glossy and uncharged with static electricity. 35

In this example, the polymer obtained in accordance with Example 4 can be replaced by the same amount of one of the polymers obtained in accordance with Examples 19 to 21 and 23 to 26.

#### EXAMPLE E.

- 40 A shampoo is prepared according to the invention by mixing the following ingredients: 40

	Sodium lauryl-ether-sulphate (2.2 mols of ethylene oxide)	14 g	
	Lauryl diethanolamide	3 g	

	Copolymer obtained in accordance with Example 2	1 g	
	Perfume	0.15 g	
	Colorant	0.2 g	
	Water q.s.p.	100 g	
5	The pH of this composition is adjusted to 7.5 by adding lactic acid.		5

## EXAMPLE F.

A pre-shampoo composition is prepared according to the invention by mixing the following ingredients:

	Copolymer obtained in accordance with Example 6	1 g	
10	Trimethylcetylammmonium bromide	1 g	10
	Propylene glycol q.s.p.	100 g	

The pH of this composition is 7.2.

This product is applied before shampooing. After waiting for a few minutes, it is rinsed out. The wet hair is easier to comb out. After shampooing and wave-setting, the hair is full of life and easy to style.

In this example, the polymer obtained in accordance with Example 6 can be replaced by the same amount of one of the polymers obtained in accordance with Examples 27 to 34 and 53 to 62.

## EXAMPLE G.

A hair-treatment cream is prepared according to the invention by mixing the following ingredients:

	Cetyl-stearyl alcohol oxyethyleneated with 2 mols of ethylene oxide, sold under the Registered Trade "BRIJ 72" by Messrs. Atlas	18 g	
25	Polymer obtained in accordance with Example 1	1 g	25
	Water q.s.p.	100 g	

60 to 80 g of this cream are applied to clean, damp hair which has been towel-dried, so as to impregnate and cover the whole head of hair.

After waiting for 15 to 20 minutes, the cream is rinsed out. The wet hair is soft and easy to comb out. After setting the hair in waves, it is easy comb out and has a silky feel.

Furthermore, the hair is glossy, full of life and has body and volume.

In this example, the polymer obtained in accordance with Example 1 can be replaced by the same amount of one of the polymers prepared in accordance with Examples 29 to 42.

## EXAMPLE H.

A dyeing carrier in the form of a cream is prepared according to the invention by mixing the following ingredients:

	Cetyl alcohol	18 g	
40	Ammonium lauryl-sulphate (30% of active materials)	12 g	40
	Oxyethyleneated stearyl alcohol containing 15 mols of ethylene oxide	3 g	
	Lauryl alcohol	5 g	
	Copolymer obtained in accordance with Example 2	3 g	

	22°B strength ammonia solution	12 ml	
	Dyestuff m-diaminoanisoie sulphate	0.048 g	
	Resorcinol	0.420 g	
	m-Aminophenol base	0.150 g	
5	Nitro-para-phenylenediamine	0.085 g	5
	Para-tolylenediamine	0.004 g	
	Ethylenediaminetetraacetic acid	1 g	
	Sodium disulphite d = 1.3	1.2 g	
	Water q.s.p.	100 g	
10	30 g of this formulation are mixed with 45 g of hydrogen peroxide of 20 volumes strength. A thick smooth cream is obtained which is pleasant to apply and adheres well to the hair.		10
	This cream is applied to the hair using a paint brush and, after waiting for 30 minutes, is then rinsed out.		
15	The hair is easy to comb out and has a silky feel.		15
	On 100% white hair, a blond shade is obtained.		
	In this example, the polymer obtained in accordance with Example 2 can be replaced by the same amount of one of the polymers prepared in accordance with Examples 35, 42 and 53 to 62.		
20	EXAMPLE I.		20
	A structuring lotion is prepared according to the invention by mixing the following ingredients at the time of use.		
	Dimethylolethylenethiourea	1.6 g	
	Copolymer obtained in accordance with Example 1	1.2 g	
25	Hydrochloric acid q.s.p. p.H. = 2.7		25
	Water q.s.p.	100 ml	
	This lotion is applied to hair which has been washed and towel-dried, before setting it in waves.		
30	After wavesetting, the hair is glossy and full of life, it has body and volume and it is silky and easier to comb out.		30
	In this example, the copolymer obtained in accordance with Example 1 can advantageously be replaced by 0.5 g of the copolymer obtained in accordance with Example 2, an excellent result is also obtained.		
35	EXAMPLE K.		35
	An aerosol lacquer is prepared according to the invention by mixing the following ingredients:		
	Copolymer obtained in accordance with Example 28	6.5 g	
	Perfume	0.2 g	
	Ethanol q.s.p.	100 g	
40	25 g of this composition are packaged in an aerosol container together with 45 g of trichlorofluoromethane and 30 g of dichlorodifluoromethane.		40
	A film of excellent quality is thus formed after spraying. The hair is glossy and soft to the touch.		
	In this example, the polymer obtained in accordance with Example 28 can be		

### EXAMPLE L.

5

5 g

0.07 g

100 g

10

10

15

**EXAMPLE M.**

20

0.6 g

20

**0.3 g**

Compound of the formula:



25

25

100 g

**EXAMPLE N.**

30

**0.6 g**

0.4 g



35

35

100 g

### EXAMPLE O.

A shampoo is prepared according to the invention by mixing the following ingredients:



Polymer obtained in accordance with Example 1.

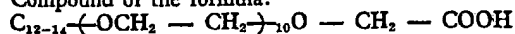
0.7 g

Vinyl acetate/crotonic acid/vinyl neodecanoate polymer  
sold by Messrs. NATIONAL STARCH under the name  
"Resin 28 29 30" neutralised with sodium hydroxide

0.35 g

5

Compound of the formula:



10 g

5

Sodium hydroxide q.s.p. pH = 9.2

Water q.s.p.

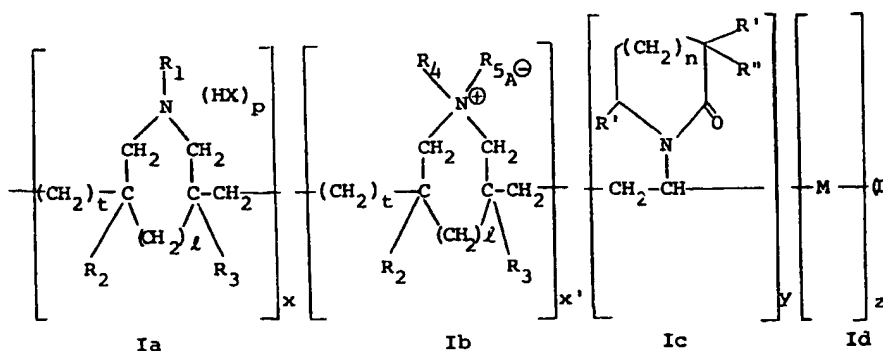
100 g

WHAT WE CLAIM IS:—

10

1. A method for treating the skin or hair which comprises applying thereto a cosmetic composition which contains, in an appropriate cosmetic carrier, at least one copolymer corresponding to the following general formula:

10



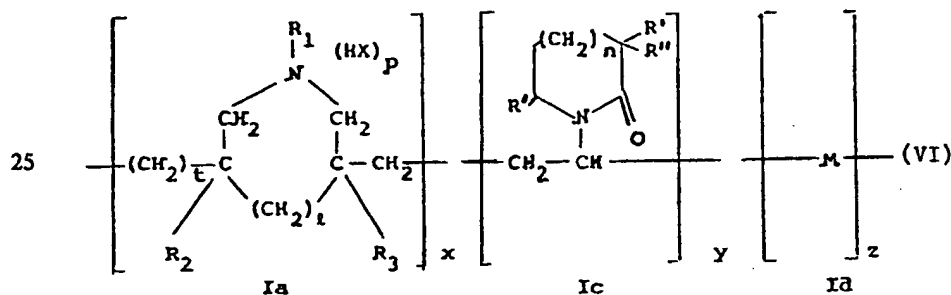
15

in which: each of  $R_1$ ,  $R_4$  and  $R_5$ , which are identical or different, represents an alkyl radical having from 1 to 12 carbon atoms, each of  $R_2$  and  $R_3$ , which are identical or different, represents a hydrogen atom or a methyl radical, each of  $R'$  and  $R''$ , which are identical or different, represents a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms,  $l = 0$  and  $t = 1$  or  $l = 1$  and  $t = 0$ ,  $n$  is 0, 1 or 2,  $p$  is 0 or 1,  $A$  represents an anion,  $HX$  is an inorganic or organic acid and  $M$  represents a unit of a polymerisable unsaturated monomer,  $x + x'$  corresponding to 95—5 mol%, it being possible for  $x + x'$  to be 0,  $y$  corresponding to 5—95 mol% and  $z$  corresponding to 0—60 mol%,  $(x + x') + y + z$  being equal to 100 mol%.

15

20

2. A method according to claim 1, in which the copolymer corresponds to the following general formula:



25

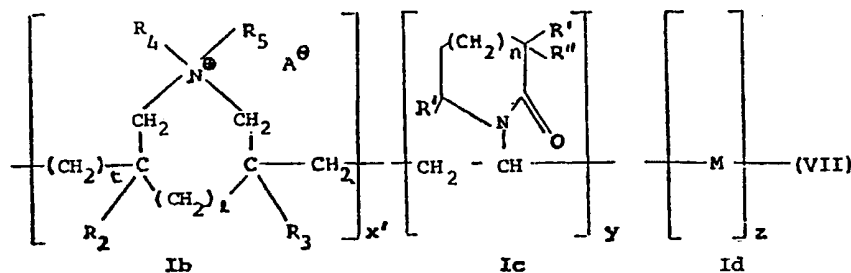
in which:  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R'$ ,  $R''$ ,  $M$ ,  $HX$ ,  $l$ ,  $t$ ,  $p$  and  $n$  are as defined in claim 1,  $x$  corresponding to 95—5 mol%,  $y$  corresponding to 5—95 mol% and  $z$  corresponding to 0—60 mol%.

25

30

3. A method according to claim 1 in which the copolymer corresponds to the following general formula:

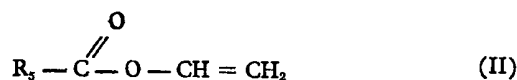
30



in which:  $R_2, R_3, R_4, R_5, R', R'', M, A, l, t$  and  $n$  are defined in claim 1,  $x'$  corresponding to 95—5 mol%,  $y$  corresponding to 5.95 mol% and  $z$  corresponding to 0.60 mol%.

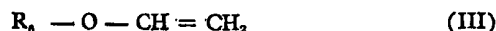
4. A method according to any one of claims 1 to 3, in which the units  $M$  are derived from an unsaturated monomer which is:

(i) a vinyl ester of the formula:



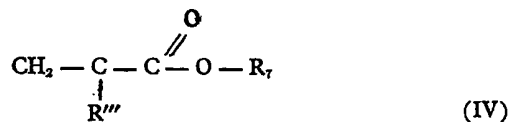
in which  $R_s$  represents an alkyl radical having from 1 to 7 carbon atoms,

(ii) a vinyl ether of the formula:

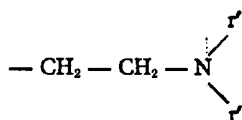


in which  $R_6$  represents an alkyl radical having from 1 to 16 carbon atoms,

(iii) an acrylic or methacrylic ester of the formula:

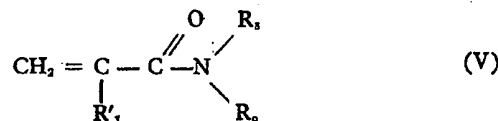


in which:  $R'''$  represents either a hydrogen atom or a methyl radical and  $R_7$  represents a linear or branched alkyl radical having from 1 to 18 carbon atoms, an alkyl radical which has from 1 to 3 carbon atoms and is substituted by at least one alkoxy having from 1 to 4 carbon atoms, or a radical of the formula:



in which each of  $r'$  and  $r''$ , which are identical or different represents an alkyl radical having from 1 to 4 carbon atoms, or

(iv) an acrylamide or methacrylamide of the formula:



in which each of  $R_8$  and  $R_9$ , which are identical or different represents a hydrogen atom or a linear or branched alkyl radical having from 1 to 4 carbon atoms, or a radical  $-(CH_2)_m - OH$ ,  $m$  being equal to 1, 2 or 3, and  $R'_1$  represents either a hydrogen atom or a methyl radical.

5. A method according to any one of claims 1 to 4, in which the units  $M$  are derived

from at least one of vinyl acetate, vinyl propionate, vinyl butyrate, vinyl laurate or vinyl stearate.

5 6. A method according to any one of claims 1 to 4, in which the units M are derived from at least one methyl vinyl ether, ethyl vinyl ether, isopropyl vinyl ether, ethylhexyl, vinyl ether, dodecyl vinyl ether or hexadecyl vinyl ether. 5

7. A method according to any one of claims 1 to 4, in which the units M are derived from at least one of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, 2-methylbutyl, 3-methylbutyl, 2-ethylbutyl, amyl, 3-methylhexyl, 3-ethylhexyl, 2-ethylhexyl, 2-methoxyethyl or 2-ethoxyethyl acrylate or methacrylate, or 2-(N,N-dimethylamino)-ethyl or 2-(N,N-diethylamino)-ethyl acrylate or methacrylate, optionally quaternised with dimethyl sulphate or ethyl bromide. 10

8. A method according to any one of claims 1 to 4, in which the units M are derived from at least one of acrylamide, methacrylamide, N-methylacrylamide, N-tert-butylacrylamide, N-hydroxymethylacrylamide, N-(1,1-dimethyl-2-hydroxy)-ethyl-1-acrylamide or N,N-dimethyl-, N,N-diethyl-, N,N-di-N-butyl- or N,N-diisobutyl-acrylamide or -methacrylamide. 15

9. A method according to any one of the preceding claims in which A represents a chloride or bromine ion.

10. A method according to any one of the preceding claims in which HX represents hydrochloric, hydrobromic acetic or lactic acid. 20

11. A method according to any one of the preceding claims, in which the copolymer has a weight average molecular weight of 2,000 to 500,000.

12. A method according to claim 11 in which the copolymer has a weight average molecular weight of 4,000 to 75,000. 25

13. A method according to any one of the preceding claims, in which the copolymer is present in the composition at a concentration of 0.01 to 15% by weight. 25

14. A method according to claim 13 in which the copolymer is present in the composition at a concentration of 0.1 to 10% by weight. 30

15. A method according to any one of the preceding claims, in which the cosmetic carrier is such that the composition is in the form of an aqueous, alcoholic or aqueous-alcoholic solution, a cream, a gel or an emulsion. 30

16. A method according to any one of the preceding claims in which the composition is in the form of an aqueous or aqueous-alcoholic solution of a lower alkanol, the composition having a pH of 6 to 8 and constituting a treatment composition. 35

17. A method according to any one of claims 1 to 16 in which the composition contains a cationic, non-ionic or anionic detergent and constitutes a shampoo.

18. A method according to claim 17, in which the detergent is present in the composition at a concentration of 5 to 50% by weight. 40

19. A method according to any one of claims 1 to 15, in which the composition is in the form of an aqueous, alcoholic or aqueous-alcoholic solution of a lower alkanol, the copolymer concentration being from 0.1 to 5% by weight and the composition constituting a wavesetting lotion.

20. A method according to any one of claims 1 to 15, in which the composition is in the form of a cream containing a dyestuff, the composition constituting a dyeing composition. 45

21. A method according to any one of claims 1 to 15, in which the composition is in the form of aqueous-alcoholic solution containing a propellant which is liquefied under pressure, the composition being packaged in an aerosol container and constituting an aerosol lacquer. 50

22. A method according to any one of the preceding claims in which the composition contains another polymer of anionic or cationic character, at a concentration of 0.1 to 10% by weight.

23. A method according to claim 22, in which the said other polymer is present in the composition at a concentration of 0.02 to 5% by weight. 55

24. A method according to any one of claims 1 to 15, in which the composition is in the form of an aqueous, alcoholic or aqueous-alcoholic solution, a cream, a gel or an emulsion, the copolymer concentration being from 4.2 to 6% by weight, the composition constituting a treatment composition for the skin. 60

25. A method according to any one of the preceding claims in which the composition contains at least one of a perfume, colorant, preservative, thickener, stabiliser, softening agent, sequestering agent, emulsifier or sunlight filter.

26. A method according to claim 1 substantially as hereinbefore described.

27. A method according to claim 1 substantially as described in any one of Examples A to O.

5 28. A composition suitable for application to the skin or hair which comprises, in an appropriate cosmetic carrier, at least one copolymer as defined in any one of claims 1 to 12 and at least one of a perfume, colorant, preservative, thickener, stabiliser, softening agent, sequestering agent, emulsifier or sunlight filter. 5

29. A composition according to claim 28 which has a feature as defined in claims 13 or claim 14.

30. A composition according to claim 28 substantially as hereinbefore described.

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